(1) Publication number:

**0 335 404** A2

1	۲.,	_	١
ı	1	2	М

## **EUROPEAN PATENT APPLICATION**

(21) Application number: 89105663.2

(5) Int. Cl.4: C11D 1/835 , C11D 3/37

2 Date of filing: 30.03.89

3 Priority: 31.03.88 JP 79228/88

Date of publication of application: 04.10.89 Bulletin 89/40

Designated Contracting States:
AT BE CH DE ES FR GB IT LI NL SE

Applicant: LION CORPORATION
No. 3-7, 1-chome Honjyo
Sumida-ku Tokyo(JP)

2-50-1, Tenno-cho Hodogaya-ku Yokohama-shi Kanagawa(JP) Inventor: Takeda, Syouzi 6-16-11, Yatsu Narashino-shi Chiba(JP)

Representative: Henkel, Feiler, Hänzel & Partner Möhlstrasse 37 D-8000 München 80(DE)

- (54) Liquid softener composition.
- (7) A liquid softener composition comprising:
  - (A) a slightly water-soluble quaternary ammonium salt type cationic surfactant having 2 or 3 alkyl or alkenyl groups with 14 to 24 carbon atoms in the molecule;
    - (B) a carboxylic acid type anionic polymer;
    - (C) a polyoxyethylene adducted nonionic surfactant; and
    - (D) an aqueous vehicle,

wherein the weight ratio of (A)/(C) is within range of from 100/1 to 3/1.

EP 0 335 404 A2

### LIQUID SOFTENER COMPOSITION

### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

The present invention relates to a softener composition which can impart, for example, an excellent softeness and antistatic property to fiber, clothing, and hair. More specifically, it relates to an aqueous liquid softener composition which can impart an excellent softeness and antistatic property to chemical textile products such as of acryl, nylon, polyester, and also has an excellent dispersion stability.

10

#### 2. Description of the Related Art

Heretofore, to prevent deterioration of the touch and antistatic properties of textile products after 15 repeated wear and washing, a softener containing a quaternary ammonium salt having two long chain alkyl groups or alkenyl groups in the molecule as the main component has been employed. Representative examples of the quaternary ammonium salts include di-hardened tallow alkyldimethylammonium chloride, and methyl-1-tallow amidoethyl-2-alkylimidazolinium methylsulfate, but these single products, although they are capable of imparting excellent softness to cotton products, have no sufficient effect from the view point of imparting softness and an antistatic property to chemical fiber products. Accordingly, proposals have been made to modify the quaternary ammonium salt itself (Japanese Unexamined Patent Publication (Kokai) No. 55-51876); use of the quaternary ammonium salt in combination with another specific di-long chain alkyl quaternary salt (Japanese Unexamined Patent Publication (Kokai) Nos. 55-51874, 55-62268, 55-103364, 55-103365); use of the quaternary ammonium salt in combination with a tri-long chain alkyl quaternary salt (Japanese Unexamined Patent Publication (Kokai) Nos. 55-112375, 55-1112377, 56-79768); use of the quaternary ammonium salt in combination with a specific mono-long chain alkyl quaternary salt (Japanese Unexamined Patent Publication (Kokai) No. 57-205581); or, use of the quaternary ammonium salt in combination with an anionic surfactant (Japanese Unexamined Patent Publication (Kokai) Nos. 53-19497, 53-38794, 53-52799, 58-13775). Nevertheless, although some improvement can be observed when these compositions are used, the effects are still unsatisfactory, or on the contrary, the softness of cotton may be worsened in some cases. Thus, up to data, a softener for domestic use which can impart a sufficient softness to both textile products of cotton and chemical fibers, and provide an excellent antistatic effect for chemical fibers, is not available.

On the other hand, the present Applicant has found that an excellent effect can be obtained by use of a carboxylic acid type anionic polymer in combination with a quaternary ammonium salt and has filed a patent application therefor (Japanese Patent Application No. 62-127722). Nevertheless, when only these two components are used, it has been found that a phase separation after a lapse of days for storage or abrupt rise in viscosity elevation occurs, whereby no sufficient dispersion stability which is essential to the commercial product cannot be satisfactorily obtained. Separately from these, proposals have been made for granular additives to a detergent by using a dilong chain alkyl quaternary ammonium salt in combination with a specific anionic polymer (Japanese Unexamined Patent Publication (Kokai) Nos. 59-6298, 61-7398), but such granular products can not be sufficiently dispersed or dissolved in water, and therefore, the object of the present invention cannot be accomplished even by using such a granular additive for the conventional washing and rinsing steps.

45

### SUMMARY OF THE INVENTION

Accordingly, an object of the present invention is to obviate the above-mentioned problems in the prior art and to provide an aqueous liquid softener composition which can impart the same softness to cotton as that of the prior art products, but a much greater softn ss and antistatic property to chemical fibers, compared with the prior art products in softening treatment practiced in the washing and rinsing steps at home, and further, has an excellent dispersion stability.

Other objects and advantages of the present invention will be apparent from the description set forth hereinbelow.

In accordance with the present invention, there is provided a liquid softener composition, comprising:

- (A) a slightly water-soluble quaternary ammonium salt type cationic surfactant having 2 or 3 alkyl or alkenyl groups with 14 to 24 carbon atoms in the molecule;
  - (B) a carboxylic acid type anionic polymer;
  - (C) a polyoxyethylene adducted nonionic surfactant; and
  - (D) an agueous vehicle, with the weight ratio of (A)/(C) being within range of from 100/1 to 3/1.

10

5

### DESCRIPTION OF THE PREFERRED EMBODIMENT

It has been found that the above-mentioned object of the present invention can be accomplished by using a specific slightly water-soluble quaternary ammonium salt type cationic surfactant in combination with a carboxylic acid type anionic polymer and a polyoxyethylene adducted nonionic surfactant.

The slightly water-soluble quaternary ammonium salt of the component (A) usable in the present invention may be exemplified by those represented by the formula (I) or (II) shown below. These compounds can be used alone or as a mixture of two or more compounds, and these are cationic surfactants having 2 or 3 straight or branched alkyl or alkenyl groups with 14 to 24 carbon atoms in the molecule which may be respectively optionally substituted or intermingled with functional groups such as

25

30

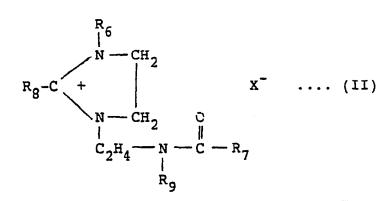
$${\binom{R_1}{R_2}} \times {\binom{R_3}{R_4}}^{+} \times {-} \qquad \dots \qquad (1)$$

wherein at least two groups of R<sub>1</sub> - R<sub>4</sub> represent straight or branched alkyl or alkenyl groups which may be unsubstituted or optionally substituted by

the remainder of the groups of  $R_1$  -  $R_4$  represent an alkyl group with 1 to 3 carbon atoms, a hydroxyalkyl group or a group represented by the formula -( $C_2H_4$ ) $_{\ell}H$  (where  $\ell$  is an integer of 1 to 5, and X represents a halogen or a monoalkylsulfate group represented by  $R_5SO_4$  where  $R_5$  represents an alkyl group with 1 to 3 carbon atoms).

40

45



50

wherein R<sub>5</sub> represents an alkyl group with 1 to 4, preferably 1 to 2 carbon atoms, R<sub>7</sub> and R<sub>8</sub> each represent an alkyl or alkenyl group with 14 to 24 carbon atoms, R<sub>9</sub> represents hydrogen or an alkyl group with 1 to 4 carbon atoms, and X has the same meaning as in the formula (I).

At least two groups of  $R_1$  -  $R_4$  in the above formula (I) have 14 to 24, preferably 16 to 22 carbon atoms,  $R_7$  and  $R_8$  in the above formula (II) have 14 to 24, preferably 15 to 21 carbon atoms, each group may have

a distribution within these ranges, and the respective groups may be either the same or different from each other. When the carbon number is lower than this range, for example, when a mixture of quaternary ammonium salts of (I) or (II) synthesized from coconut fatty acids is used, the softness will be poor.

Specific examples of the component (A) include one or a mixture of two or more of di-hardened tallow alkyldimethylammonium chloride, di-tallow alkyldimethylammonium bromide, dioleyldimethylammonium chloride, dipalmitylhydroxyethylammonium methylsulfate, distearylmethylpolyoxyethylene (average degree of colymerization is 3)ammonium chloride, diisostearyldimethylammonium methylsulfate, dieicosyldimethylammonium chloride, dibehenylmethylpolyoxyethylene (average degree of polymerization is 5)ammonium chloride, dierucyldimethylammonium chloride, di[2-dodecanoylamino)ethyl]-dimethylammonium di[2-stearoylamino)propyl]dimethylammonium ethylsulfate, di(2-ethylpalmitoyl)hydroxyethylmethylammonium methylsulfate, trioleylmethylammonium chloride, dioleylmonostearylmethylammonium chloride, dioleylmonobehenylmethylammonium chloride, monooleyldierucylmethylammonium chloride, tristearylmethylammonium methylsulfate, methyl-1-tallow amidoethyl-2-tallow alkylimidazolinium methylsulfate, methyl-1-hexadecanolylamidoethyl-2-pentadecylimidazolinium chloride, ethyl-1-octadecenoylamidoethyl-2-heptadecenylimidazolinium ethylsulfate, and the like. The content of the component (A) in the softener composition may be as desired but is preferably 3 to 50% by weight (hereinafter abbreviated merely as %), more preferably 4 to 20%.

As the carboxylic acid type anionic polymer of the component (B), homopolymers of ethylenically unsaturated carboxylic acids or anhydrides thereof or copolymers of said monomers can be used. The salts of these homopolymers and copolymers may be used. Also, these polymers may be used either as such or in the form of water soluble neutral salts such as alkali metal salts or alkaline earth metal salts. The component (B) has an average molecular weight generally of 500 to 50,000, preferably 500 to 20,000, and more preferably 500 to 10,000.

The above-mentioned anionic polymrs to be used as the component (B) should be the so-called "oligomers" which have a relatively low molecular weight. When the molecular weight thereof is higher, the desired sufficient dispersion stability obtained from the addition of the component (C) as mentioned hereinbelow is prevented. Contrarily, when the molecular weight is lower, the effect obtained from addition of the component (B) as mentioned hereinbelow becomes insufficient.

Specific examples of the component (B) may include one or a mixture of two or more of polyacrylic acid, polymethacrylic acid, polycrotonic acid, polyacotinic acid, poly- $\alpha$ -hydroxyacrylic acid, polymaleic acid, polysorbic acid, polyitaconic acid, poly(maleic anhydride), poly(itaconic anhydride) their copolymers, or salts of these homopolymers or copolymers.

In the liquid softener composition, the reason why excellent effect can be obtained by using the component (A) and the component (B) in combination is not clear, but it may be considered to be as follows. That is, although the ion bonding between the both may not be so strong, by forming a cation-anion complex with a part of the dispersed particles of the component (A), the component (A) can be made further hydrophobic to promote adsorption of the component (A) onto chemical fibers such as acrylic or polyester fibers which are hydrophobic fibers, whereby softness and antistatic property of the chemical fibers can be consequently further improved as compared with the case of the component (A) alone. On the other hand, the component (B) which is a water soluble polymer will not be incorporated into the dispersed particles of the component (A) and will not destroy the adsorption structure of the component (A), as different from a some kinds of anionic surfactant, and consequently will not give any adverse effect on the softness of cotton fibers.

In view of the above mechanism, it is important to control the amount of the component (B) formulated as the relative value to the component (A). Specifically, these compounds are formulated, in terms of the ratio of positive charge mols (a) of the component (A) to the negative charge mols (b) of the component (B), at a ratio (a)/(b) of 1/0.2 to 1/2.0, preferably 1/0.5 to 1/1.0. If the ratio of the component (B) to the component (A) is outside this range, the above effect of combined use is difficult to obtain.

The third essential component for accomplishing the object of the present invention is the component (C). That is, a sufficient dispersion stability is an essential condition for use as a softener for domestic use, but only with the components (A), (B), (D), the required dispersibility cannot be obtained, and accordingly the emulsifying stabilizing action of the component (C) is necessary.

The component (C) usabl in the present invention may be exemplified by polyoxyethylene alkylphenyl ether, polyoxyethylene alkyl (or alkenyl) ether, polyoxyethylene fatty acid amide, polyoxyethylene alkyl (or alkenyl) amine, and polyoxyethylene sorbitane fatty acid ester. Preferable average additional moles of ethylene oxide are at least 20, more preferably 20 to 100. Examples of such a component (C) are POE ( $\bar{p}$  = 20 - 100) alkyl (C<sub>8-12</sub>)phenyl ether, POE( $\bar{p}$  = 20 - 100) alkyl or alkenyl (C<sub>10-20</sub>) amine, or mixtures ther of. In the above compounds, ach POE represents

polyoxyethylene, p denotes the average adducted mols of ethylene oxide, and C the carbon number of the alkyl or alkenyl group (hereinafter the same).

The component (C) improves the emulsifying dispersion of the dispersed particles of the component (A) alone and the anion-cation complex of the dispersed particles of the component (A) with the component (B), which may be considered to form a random coil structure dissolved in the aqueous phase in the composition, and thus the amount of the component (C) formulated is preferably 100/1 to 3/1 as a weight ratio of (A)/(C), more preferably 50/1 to 5/10. If the ratio of the component (C) to the component (A) is outside of this range, the above effect cannot be exhibited, and conversely, the above effect of combined use of the component (A) and the component (B) is frequently inhibited.

The component (D) is used as the carrier for the essential components and the optional components of the present invention, and the amount thereof in the composition is the balance which makes up the total amount to 100%, in addition to the essential components and the optional components formulated.

The softener composition of the present invention can include optional components in addition to the above essential components, including viscosity controllers such as inorganic electrolytes like sodium chloride, potassium chloride, magnesium chloride, aluminum chloride, sodium sulfate, ammonium sulfate, sodium nitrate, or magnesium nitrate; and polyethylene glycol or other water soluble organic polymers; hydrotropes such as lower alcohols like ethanol, or isopropanol, ethylene glycol, glycerine, and urea; and pH controllers, sterilizers, pigment dyes, perfumes, antioxidants, UV-ray absorbers, and fluorescent brighteners.

The softener composition of the present invention can be prepared according to known methods. More specifically, it is desirable that the component (A) should be finely and uniformly dispersed, and for this purpose, it is preferable to use the method in which the components (B), (C) and optical components are previously dissolved in an aqueous vehicle, and to this solution is successively added, under heating to 40°C to 80°C if desired, the component (A) in a molten state to be mixed under stirring. On the other hand, when optional components susceptible to denaturation at high temperature are used, it is desirable to cool the above dispersion to about room temperature, followed by addition while stirring. A pH controller can be added to the softener composition of the present invention, but the pH of the composition is not limited. Usually, the pH is that when the respective components are formulated, but it is desirable to control pH to 4 to 8. For this purpose, an organic or inorganic acid or a basic compound can be formulated, as desired.

The softener composition of the present invention which can impart an excellent softness to not only cotton fibers but also chemical fibers, and further gives an excellent antistatic property to chemical fibers is valuable

Also it has excellent freeze-tham stability, whereas it shows neither remarkable viscosity rise nor abnormal phase separation even when stored for a long term. Thus, the present composition is excellent in practical application.

## **EXAMPLES**

40

10

The present invention now will be further illustrated by, but is by no means limited to, the following examples.

The preparation, performance evaluation and dispersion stability evaluation of the softener compositions in Examples were conducted according to the following methods.

45

### Method of Preparation of Aqueous Dispersion:

Other components except for the component (A) were dissolved in water, the resultant solution was heated to 45°C and to this was added dropwise under stirring the molten product of the component (A) to be dispersed uniformly, followed by cooling to 25°C.

#### Finishing Treatment Method:

55

Commercially available cotton towel, acrylic cloth were washed repeatedly twice with a commercially available detergent for clothing by means of an electric washing machine at 50°C, and then thoroughly rinsed with tap water at normal temperature to provide test cloths.

Next, into 30 liters of tap water of 25°C was added the softener composition to an amount of the component (A) added of 1 g to form a uniform solution. Each test cloth was dipped in this solution at a bath ratio of 30-fold to carry out the treatment for 3 minutes, and then dehydrated for 2 minutes. The cloth thus treated was dried on air, and then the cotton towel for evaluation of softening effect was left to stand under the conditions of 25°C, 65% RH for 24 hours, while the acrylic cloth for evaluation of antistatic effect under the conditions of 20°C, 50% RH for 72 hours, before use for the respective evaluation tests.

## Performance Evaluation Method:

10

- (a) Softness: Touch feelings of cotton towel before and after treatment were compared and evaluated according to the following standards:
- + 5 ..... very soft
- + 4 ..... considerably soft
- 15 + 3 ..... soft
  - + 2 ..... some softness
  - + 1 ..... slightly soft
  - 0 ..... unchanged, as before treatment;
- (b) antistatic property: By means of a static honestometer (manufactured by Shishido Shokai), the polyester cloth was charged at an application voltage of 7 KV at a target distance of 20 mm, and the half life (sec.) of the residual voltage after the removal of the applied voltage was measured.

## Method of Evaluation of Dispersion Stability:

25

- (a) viscosity change: The viscosities for each softener composition prepared, one composition immediately after preparation, one freezed at -15 °C for 40 hours and then thawed at 25 °C and one stored at 45 °C for one month were measured by means of a B type viscometer (manufactured by Tokyo Keiki) (measurement was conducted at 25 °C);
- (b) judgement of phase separation: each softener composition prepared was charged into a transparent cylinder bottle of 45 mm in inner diameter to 70 mm from the bottom of the bottle, stationarily stored at 5 °C for one month, and then the separated length was measured. Evaluation:
- o: not separated
- Δ: separated length less than 3 mm
- 5 x: separated length of 3 mm or longer

## Example 1

Various liquid softener compositions with various liquid properties shown below were prepared, and their performances and dispersion stabilitis thereof were evaluated. The results are shown in Table 1.

	Component (	A):	di-hardened tallow alkyldimetyl-
45			ammonium chloride: 5%
	Component (	B):	(Polymer shown in Table 1)
		:	[equivalent in charge molar ratio
50			to component (A)]
50	Component (	C):	POE (p=40) nonylphenyl ether
		:	0.25% [(A)/(C) weight ratio=20/1]
	Component (	D):	3% aqueous ethylene glycol

55

## balance.

5	The above component (A) is were contaminated with about 1.7 (	available as	a mixture	with	isopropanol,	and	therefore,	the	compositions
		(***,							
10									
15									
20									
25							-,		
									•
30					•				
35									
40									
45									
50									
	·								
55	·								

			Phase	seps	o	o	•	o	٥	•	•
5		Disparaton stability	í.ee.)	After restored from freezing	0 4 4	140	1100	200	1200	094	550
15		Diepar	Viscosity (centipoles)	After storese (45°C, I month)	220	260	066	160	1400	330	290
20				Immediately after preparation	09	100	140	90	370	0.0	6.5
25		Ance	Antistatic property	Acrylic cloth	3 (886)	01	13	18	4	2.5	17
	-	Performance	9.8	Acrylic	<del>,</del>	+4 - +5	+4 - +5	+4 - +5	. +4 - +5	Ž.	÷
30	Table 1		Softness	Corton	ţ.	+5	+5 .	\$+	\$	÷	\$+
				Amount (1)	0.64	,0.64	99.0	0.85	0.67	0.11	0.51
35			(1		average (molecular 4,000) weight	8,000)	30,000)	7,000)	acid copolymer " 40,000)	copolymer . 9,000)	6000
40			Component (B)	Namo	average (molecul	•	•	•		acid copo	-
45			Ö	ž	Polyacrylic acid		•	Sodium polyacrylate	Acrylic acid - methacrylic Polymerization - 3:1) (molar ratio	Acrylic acid - maloic acid Polymerization - 2:1) ( molar ratio	Polymaleic acid
50			:	E		7	m	•	'n	v	
55				•	Present products						

		Phase	sepa-	0	•	
5	Dispersion stability	100)	After restored from fracting	1160	730	
10	Dieper	Viscosity (centipolee)	Immediately After storage after (45°C, preparation 1 month)	1340	880	-
20			Immediately after preparation	280	230	•
oc <b>d</b>	anc e	Antistatic property	Acrylic	25	07	> 300
Table 1 (continued)	Performance	<b>8</b>	Gotton Acrylic towel cloth	\$ <del>+</del> .	7	0
30		Softness		+5	÷	0
린			Amount (1)	0.76		The second secon
35				8,000)		
40		Component (B)	Name	. ;		
45				Polycrotonic acid	(No addition)	(untrested)
50			2	0d. 190	6	
55			,	Present Products	Compan	stive example

From Table 1, it can be understood that the softener compositions of the present invention have excellent performance and dispersion stability. More specifically, although considerable softness is exhibited in the case of di-hardened tallow alkyldimethylammonium chloride alone, the softness and antistatic property of the acrylic cloth are clearly improved by addition of the component (B). Particularly, No. 1 and No. 5 can be appreciated to exhibit a very excellent antistatic property. Also, according to the experience of the present inventors, a rise in viscosity under the above storage conditions may be permissible up to about 1500 centipoise in commercial product value, and it can be seen that the products of the present invention satisfy this condition without causing phase separation due to the addition effect of the component (C) and the presence of ethylene glycol in the component (D).

## Example 2

Various softener compositions were prepared to a charge molar ratio (a)/(b) of the component (A) and the component (B) of 1/0.8, and their performances and dispersion stabilitis thereof were evaluated. The results are shown in Table 2.

	40 45	35	S Table 2	25 NI	20		15	10	5
1				Pres	Present products	ıcts		Comparative	itive
			No.	10	11	12	13	14	15
Component (A)		Di-hardened tallow alkylaimethyl- ammonium chloride	thy1-	0.4	0.6	12.0	5.0	5.0	5.0
Component (B)	Polymale acid	average (molecular 1 weight	1500)	0.33	0.73	0.98	17.0	0.41	0.41
Component	POE(p-30)	octylphenyl ether		0.04	•	•	ı	ı	1
	POE(p=50)	oleyl ether		1	3.0	1	ı	•	ı
	POE(p=60) tall	tallow alkylamine		t	,	2.4	ì	1	1
	$POE(\bar{p}=40)$ sec- $(C_{12} - C_{14})$	sec-alkyl ether )		1	ı	•	0.1	0.44	2.0
Component	Ethylene glycol	5]		5.0	6.0	10.0	4.0	4.0	4.0
	Sodium chloride	je je		i	0.2	0.4	1	1	1
	Acetic acid			•	•	0.05	•	ı	•
	Deionized water	นอ		balance	balance	balance	balance	balance	balance
hod	Component (A)/Component (C) ratio			100/1	3/1	5/1	50/1	125/1	2.5/1

5			
10			
15			
20			
25 :			
30		•	
35			
40			
45			
50			

120::024		,
4000		֡
•	•	1
7		

Per- Softness Cotton formances formances Acryl: Antistatic property (sec) Acryl: persion viscosity (centipoise) Immediates sta- bility			Prese	Present products	cts		Comparative example	ative e
Softness  Antistatic property (sec)  Viscosity (centipoise)		No.	10	11	12	13	14	15
Antistatic property (sec) Viscosity (centipoise)	oftness	Cotton towel	+5	+5	+5	+5	+5	5+ - 7+
Antistatic property (sec) Viscosity (centipoise)		Acrylic cloth	+5	+ 5	+5	÷	+ 2	+3 - +4
Viscosity (centipoise)	$\overline{}$	Acrylic cloth	13	18	<b>o</b>	1.5	16	35
	iscosity (centipoise)	Immediately after preparation	320	80	150	280	450	15
2,64)		After stored (45°C, 1 month)	1440	360	680	076	3300	80
After from :		After restored from freezing	1300	720	870	1180	2860	130
Phase separation	hase separation		o	0	0	o	o	×

From Table 2, it can be understood that all of the products of the present invention have good performances and also excellent dispersion stability. In contrast, as shown in Comparative examples, if the ratio of the component (C) relative to the component (A) is too low, i.e., outside the range defined in the present invention (No. 14), viscosity elevation after a lapse of days for storage is marked, while if it is too much (No. 15), phase separation is liable to occur, and there is also an undesirable tendency that the performance to be improved by addition of the component (B) is contrariwise inhibited.

## Example 3

15

35

Using dioleyldimethylammonium chloride as the component (A) and varying the amount of polyacrylic acid formulated as the component (B), softener compositions shown below were prepared and their performances were evaluated. The results are shown in Table 3:

Component (A): dioleyldimethylammonium chloride (iodine value = 73): 9 (%); Component (B): polyacrylic acid (average molecular 20 weight = 1,000): 0 to about 2.3 (%); Component (C): POE (p=50) oleylamine 2 (%) [(A)/(C) weight ratio=4.5/1]; sodium chloride: 0.2(8)Component (D): glycerine: 10 (%) deionized water: balance *3*0

The above component (A), is provided as a mixture with isopropanol, and therefore, the compositions were contaminated with about 3 (%) thereof.

Table 3

40	-	No.	Amount of the component (B) (%)	Component (A)/Component (B) charge molar ratio (a)/(b)	Perfori	mance eva	luation
					Softr	ness	Antistatic property
45					Cotton towel	Acrylic cloth	Acrylic cloth
	Comparative example	16	(no addition)	1/0	+3	+3	100 (sec)
	Present products	17	0.11	1/0.1	+3	+3	80
		18	0.23	1/0.2	+3	+3	50
50		19	0.57	1/0.5	+3	+3-+4	15
-		20	0.91	1/0.8	+3-+4	+3-+4	3
		21	1.14	1/1.0	+3 - +4	+3-+4	2
		22	1.71	1/1.5	+3	+3-+4	30
		23	2.29	1/2.0	+3	+3	70
55		24	2.86	1/2.5	+3	+3	90

From Table 3, it can be understood that softness and/or antistatic property of the acrylic cloth can be improved by an addition of the component (B). Furthermore, it is also clear that the softness of the cotton

towel is improved in some cases. Thus, these effects are more marked when the charge molar ratio (a)/(b) is within the range from 1/0.2 to 1/2.0, more preferably from 1/0.5 to 1/1.0. Also all of the above compositions of the present invention have a good dispersion stability, which may be attributed to the addition effects of the component (C) and glycerine in the component (D).

## Example 4

5

40

45

50

55

Using various slightly water soluble di/tri-long chain alkyl/alkenyl quaternary ammonium salts as the component (A) and sodium polyacrylate as the component (A) at equivalent charge molar ratio (a)/(b), softener compositions with the compositions shown below were prepared and their performances were evaluated and compared with the case when sodium polyacrylate was not added. The results are shown in Table 4.

15	Component (A):	(quaternary ammonium salt listed
	2 ( )	in Table 4)
	<b>\$</b>	5.0 (%);
20	Component (B):	sodium polyacrylate (average
		molecular weight 7000)
	:	0 (%) or amount to charge molar
25		ratio (a)/(b) of 1/1;
	Component (C):	POE (p=20) branched alkyl ether
		(C <sub>13, 15</sub> branching ratio 50%)
	:	0.4 (%)
30	•	<pre>[(A)/(C) weight ratio=12.5/1]</pre>
	Component (D):	propylene glycol: 6.0 (%)
		deionized water: balance
35		

Composition   Performance	50	45	40	35	30	25	20	15	10	5
No.   Name of component (A)   Component (B) (I)   Cotton Acrylic component (B) (I)   Cotton Acrylic component (B) (I)   Cotton Acrylic cloth cloth cloth branched isostearyl)dimethyl-   0.80					<b>€-1</b>					
No.         Name of component (A)         Amount of component (B) (I)         Softness           25         Dioleyldimethylammonium chloride ammonium chloride ammonium chloride ammonium chloride         0.82         +3         +3         +4           26         Di(methyl branched isostearyl)dimethyl- o.80         +3         +4         +4           27         Dioleylmonostearylammonium chloride ammonium chloride chloride ammonium chloride         0.59         +4         +5         +3         +4           29         Di(2-tallow anidoethyl)methyl POE(p=2)         0.61         +3         +3         +4           29         Di(2-tallow anidoethyl)methyl POE(p=2)         0.61         +3         +4         +4           30         Di(2-palmitoylethyl)hydroxyethylmethyl- o.69         +3         +4         +4           31         Methyl-tallow amidoethyl-2-tallow inido- o.65         +3         +4         +4           32         (the same as No. 25)         0.65         +3         +4         +4           33         (the same as No. 25)         0         +3         +4         +4           34         (the same as No. 27)         0         +3         +4         +4					Compositio	u			Performan	sec
25 Dioleyldimethylammonium chloride 0.82 +3 +3 -44  26 Di(methyl branched isostearyl)dimethyl- 0.80 +3 -44 +4 -45  27 Dioleylmonostearylammonium chloride 0.59 +3 -44 +4 -45  28 Di-hardened tallow alkylemethyl POE(p=3) 0.69 +4 -45 +3 -44  ammonium chloride 0.69 +4 -45 +3 -44  29 Di(2-tallow amidoethyl)methyl POE(p=2) 0.61 +3 +3 -44  ammonium chloride 0.69 +4 -45 +3 -44  ammonium methylsulfate 0.69 +4 -45 +3 -44  ammonium methylsulfate 0.69 +3 +4 +4  20 Di(2-tallow amidoethyl)-2-tallow imido- 0.65 +3 -44  44 +4 +4  31 Methyl-tallow amidoethyl-2-tallow imido- 0.65 +3 -44  32 (the same as No. 25) 0 +3 -44  34 (the same as No. 25) 0 +3 -44  34 (the same as No. 27) 0 +3 -44  35 +4 +3 -44  36 +4 +3 -44  37 +4 +3 -44  38 +4 +3 -44  39 +4 +3 -44  30 +4 +3 -44  30 +4 +3 -44  31 +4 +3 -44  32 +4 +3 -44  33 +4 +3 -44  34 +4 +3 -44  35 +4 +3 -44  36 +4 +3 -44  37 +4 +3 -44  38 +4 +3 -44  39 +4 +3 -44  39 +4 +3 -44  30 +4 +3 -44  30 +4 +3 -44  31 +4 +3 -44  32 +4 +3 -44  33 +4 +3 -44  34 +4 +3 -44  35 +4 +3 -44  36 +4 -45  37 +4 +4 -45  38 +4 +4 -45  39 +4 +4 -45  40 +4 +4 -45  40 +4 +4 +4  40 +4 +4  40 +4 +4  40 +4 +4  40 +4 +4  40 +4 +4  40 +4 +4  40 +4 +4  40 +4 +4  40 +4 +4  40 +4 +4  40 +4	1	No.							10	Antistatic property
25 Dioleyldimethylammonium chloride  26 Di(methyl branched isostearyl)dimethyl- ammonium chloride  27 Dioleylmonostearylammonium chloride  28 Di-hardened tallow alkylemethyl POE(p=3)  29 Di(2-tallow amidoethyl)methyl POE(p=2)  30 Di(2-tallow amidoethyl)methyl POE(p=2)  30 Di(2-palmitoylethyl)hydroxyethylmethyl-  31 Methyl-tallow amidoethyl-2-tallow imido-  32 (the same as No. 25)  33 (the same as No. 25)  43 + 4 + 3 - 4  54 + 4  54 + 4  55 + 3 - 4  56 + 4 - +5  57 + 3 - 4  58 + 3 - 4  58 + 4 - +5  59 + 3 - 4  50 + 4 - +5  50 + 4 - +5  50 + 4 - +5  50 + 4 - +5  50 + 4 - +5  50 + 4 - +5  50 + 4 - +5  50 + 4 - +5  50 + 4 - +5  50 + 4 - +5  50 + 4 - +5  50 + 4 - +5  50 + 4 - +5  50 + 4 - +5  50 + 3 - +4  50 + 4 + +			Nam	e or compon	ient (A)		1	1	Acrylic cloth	Acrylic cloth
26 Di(methyl branched isostearyl)dimethyl- ammonium chloride  27 Dioleylmonostearylammonlum chloride  28 Di-hardened tallow alkylemethyl POE(p=3)  29 Di(2-tallow amidoethyl)methyl POE(p=2)  30 Di(2-palmitoylethyl)hydroxyethylmethyl- ammonium methylsulfate  31 Methyl-tallow amidoethyl-2-tallow imido-  32 (the same as No. 25)  33 (the same as No. 25)  44 - +5 +4 - +5  47 - +5  43 +4 - +5  43 +4 - +5  43 +4 - +5  43 +4  44 - +5  43 +4  43 - +4  44  44  44  44  44  44  44  44  44	Present	25		thylammoniu	m chloride		0.82	+	1	3 ( )
27 Dioleylmonostearylammonium chloride  28 Di-hardened tallow alkylemethyl POE(p=3)  29 Di(2-tallow amidoethyl)methyl POE(p=2)  30 Di(2-palmitoylethyl)hydroxyethylmethyl-  31 Methyl-tallow amidoethyl-2-tallow imido-  32 (the same as No. 25)  33 (the same as No. 25)  34 (the same as No. 27)  36 Di-hardened tallow and charter  37 H + 4 - +5 +3 - +4  4 - +5 +3 - +4  4 - +5  4 + - +5  4 + + - +5  4 + + - +5  4 + + - +5  4 + + - +5  4 + + - +5  4 + + - +5  4 + + - +5  4 + + - +5  4 + + - +5  4 + + - +5  4 + + - +5  4 + + - +5  4 + + - +5  4 + + - +5  4 + + + - +5  4 + + + + + + + + + + + + + + + + + +	products	26	Di(methyl bi ammonium chl		ostearyl)dí	methyl-	0.80	1	<b>5</b> +	23
29 Di(2-tallow amidoethyl) POE(p=2) 0.69 +4 - +5 +3 - +4 ammonium chloride  30 Di(2-tallow amidoethyl) methyl POE(p=2) 0.61 +3 +3 +3 +3 ammonium chloride  31 Methyl-tallow amidoethyl-2-tallow imido-  22 Cilnium methyl sulfate  32 (the same as No. 25) 0.65 +3 - +4 +4 +3 - +4 +3 - +4 +4 +4 +3 - +4 +4 +4 +4 +4 +4 +4 +4 +4 +4 +4 +4 +4		27	Dioleylmono	stearylammo	nium chlor	ide	0.59	1	- 4+	4
29 Di(2-tallow amidoethyl)methyl POE(p=2) 0.61 +3 +3 ammonium chloride  30 Di(2-palmitoylethyl)hydroxyethylmethyl- ammonium methylsulfate  31 Methyl-tallow amidoethyl-2-tallow imido- 20linium methyl sulfate  32 (the same as No. 25) 0.65 +3 - +4 +4  33 (the same as No. 25) 0 +3 - +4 +3 - +4  34 (the same as No. 27) 0 +3 - +4 +3 - +4		28	Di-hardened ammonium ch.	tallow alk loride	rylemethyl	POE(p̃=3)	0.69	1	+3	4
30 Di(2-palmitoylethyl)hydroxyethylmethyl- aumonium methylsulfate  31 Methyl-tallow amidoethyl-2-tallow imido- 20linium methyl sulfate  32 (the same as No. 25)  33 (the same as No. 25)  34 (the same as No. 27)  36 (the same as No. 27)  37 (the same as No. 27)  38 (the same as No. 27)  39 (the same as No. 27)		29	Di(2-tallow ammonium ch.	amidoethyl loride	l)methyl PC	)E(p̃=2)	0.61	+	ლ +	77
31 Methyl-tallow amidoethyl-2-tallow imido- 0.65 +3 - +4 +4		30	Di(2-palmite ammonium me	oylethyl)hy thylsulfate	/droxyethy1	lmethyl-	0.69	+	1	58
32 (the same as No. 25) 0 +3 +3 33 (the same as No. 25) 0 +3 - +4 +3 - +4 34 (the same as No. 27) 0 +3 - +4 +3 - +4		31	Methyl-tall zolinium me	ow amidoeth thyl sulfat	1y1-2-tallc	w imido-	0.65	1		9
33 (the same as No. 25) 0 +3 - +4 +3 - +4 3 - +4 34 (the same as No. 27) 0 +3 - +4 +3 - +4	Compar-	32	same	No.			0	+3	+3	100
(the same as No. 27) 0 +3 - +4 +3 - +4	ative example	33	same	No.			0		+3 -	7.5
		34	same	No.			0	1	+3 -	43

5	ances	Antistatic property	c Acrylic cloth	2.5	220	140	110
10	Performances		Acrylic cloth	<b>5</b> +	+5	+3	+3
15		Softness	Cotton towel	+4 - +5	+5	+2	+3 - +4
20 <b>(</b>		Amount of	component (B) (I)	0	0	0	0
continue							
Table 4 (continued)	Composition	Composition of component (A)	Name of component (A)				
35				as No. 28)	No. 29)	as No. 30)	as No. 31)
40			Ивте	(the same as	(the same as	(the same as	(the same as
45		No.		35	36	37	38
50		•		Compar-	ative example		

From Table 4, it can be understood that the carboxylic acid type anionic polymers used in the present invention have performance improvement effects on all of the slightly water soluble quaternary ammonium saits having different structures from each other. More specifically, in Table 4, it can be seen that by an addition of sodium polyacrylate in equivalent amount to the component (A), in all cases, the performances,

particularly softness and antistatic property of the acrylic cloths are greatly improved. Also, all of the above compositions of the present invention have good dispersion stability.

### 5 Claims

10

15

20

35

40

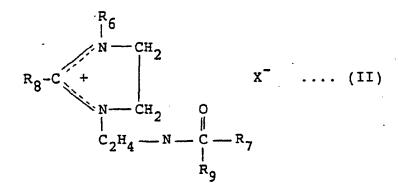
45

- 1. A liquid softener composition comprising:
- (A) a slightly water-soluble quaternary ammonium salt cationic surfactant having 2 or 3 alkyl or alkenyl groups with 14 to 24 carbon atoms in the molecule;
  - (B) a carboxylic acid anionic polymer;
  - (C) a polyoxyethylene adducted nonionic surfactant; and
- (D) an aqueous vehicle, with the weight ratio of the components (A)/(C) being within range of from 100/1 to 3/1.
- 2. A liquid softener composition as claimed in claim 1, wherein said slightly water-soluble quaternary ammonium salt cationic surfactant (A) is at least one component selected from the group consisting of the cationic surfactants having the formulae (I) and (II):

$${\binom{R_1}{R_2}} {\binom{R_3}{R_4}}^+ x^- \dots (I)$$

wherein at least two groups R<sub>1</sub> through R<sub>4</sub> represent straight or branched alkyl or alkenyl groups which may be unsubstituted or optionally substituted with

the remainder of the groups of  $R_1$  -  $R_4$  represent an alkyl group with 1 to 3 carbon atoms, a hydroxyalkyl group or a group represented by the formula -( $C_2H_4$ ) $_1H$  where 1 is an integer of 1 to 5, and X represents a halogen or a monoalkylsulfate group represented by  $R_5SO_4$  where  $R_5$  represents an alkyl group with 1 to 3 carbon atoms.



wherein R6 represents an alkyl group with 1 to 4, preferably 1 to 2 carbon atoms,  $R_7$  and  $R_8$  each represent an alkyl or alkenyl group with 14 to 24 carbon atoms,  $R_9$  represents hydrogen or an alkyl group with 1 to 4 carbon atoms, and X has the same meaning as in the formula (I).

- 3. A liquid softener composition as claimed in claim 1, wherein the amount of the component (A) is 3 to 50% by weight.
- 4. A liquid softener composition as claimed in claim 1, wherein said carboxylic acid anionic polymer (B) is at least one polymer selected from the group consisting of homopolymers of ethylenically unsaturated carboxylic acids and anhydrides thereof and their copolymers and saits of said homopolymers and copolymers.
- 5. A liquid softener composition as claimed in claim 1, wherein said carboxylic acid anionic polymer (B) has an average molecular weight of 500 to 50000.



# EUROPEAN SEARCH REPORT

EP 89 10 5663

	Citation of document with indica	tion, where appropriate,	Relevant	CLASSIFICATION OF THE	
ategory	of relevant passage	s	to claim	APPLICATION (Int. Cl.4)	
(	DE-A-2459125 (CIBA-GEIGY AC * claims 1, 8, 10 *	3)	1-2	C11D1/835 C11D3/37	
	US-A-3537993 (T.L. COWARD   * column 1, line 10 - colum * column 4, lines 63 - 70	mn 3, line 17 *	1-4, 7		
`	FR-A-2407261 (UNILEVER) * page 4, 1ine 10 - page 5	, line 33; claim 1 *	1-2, 4-5, 7		
	GB-A-2151252 (SANDOZ LTD) * claims 1, 3 *		1, 4-5, 7		
				·	
		·		TECHNICAL FIELDS SEARCHED (Int. Cl.4)	
	,		C11D		
1	The present search report has been d	trawn up for all claims			
	Place of search	Date of completion of the search		Exceptiver	
THE HAGUE		23 OCTOBER 1990	23 OCTOBER 1990 SERB		
X : part Y : part	CATEGORY OF CITED DOCUMENTS icularly relevant if taken alone icularly relevant if combined with another ument of the same category	T: theory or principle E: earlier patent doc after the filing da D: document cited in L: document cited	ument, but publ to the application	ished on, or	